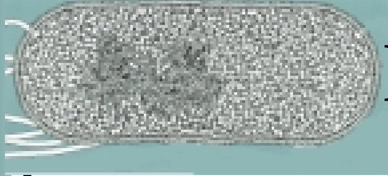


# Diffusion, Fields and Their Uses

**Topics for today's lecture:**

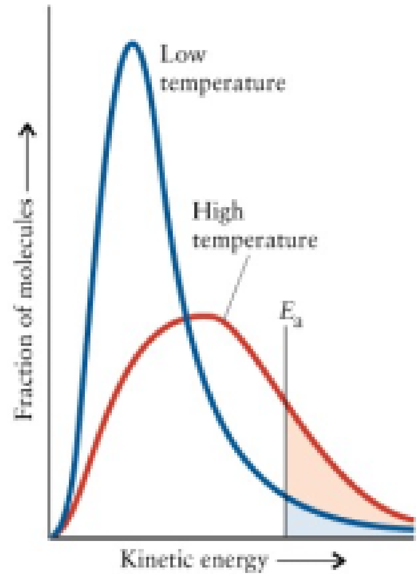
*Random Walks*
*Fick's Laws*
*Diffusion*
*Frictional Coefficients*

Plugging these values back into our original equation for $dn_c$

$$dn_c = 4\pi N B^3 c^2 e^{-\beta c^2} dc$$

We get:

$$\frac{1}{N}\frac{dn_c}{dc} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$



To calculate the average speed of a molecule:

$$< c >= \int_0^\infty c \frac{1}{N} \frac{dn_c}{dc} dc = \int_0^\infty c P(c) dc$$

Using equations like this is it straightforward to derive:

$$< c >= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$< c^2 >= \frac{3kT}{m}$$

$\lambda = \langle c \rangle / Z_1$

$Z_1 = (0.5)^{1/2} \pi \sigma^2 \langle c_{rel} \rangle * N/V$

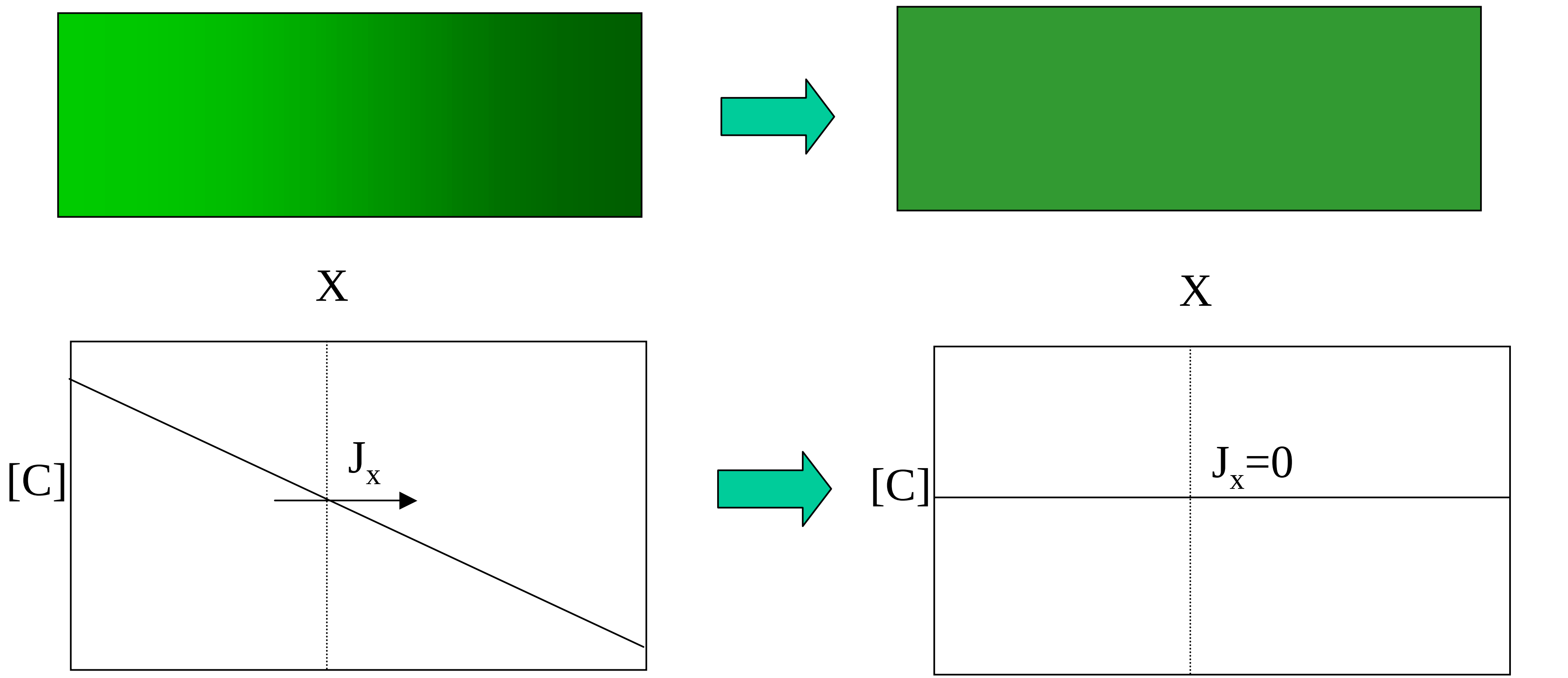
$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \frac{N}{V}}$$

Thus the mean free path is dependent on molecular radius and the density of the gas.

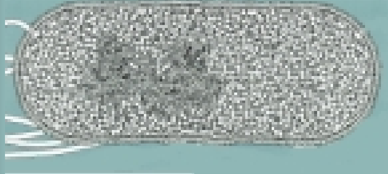
At each collision the particle will be deflected off in another direction.

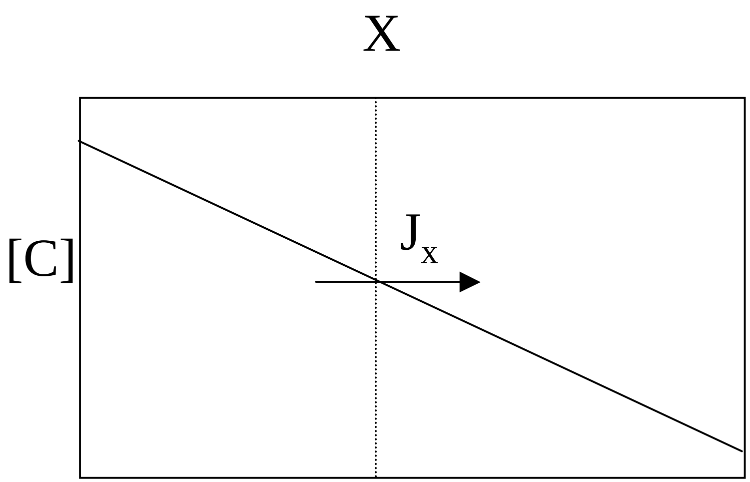
How long does it take a particle to move a given distance from a starting point?

Now all this moving about tends to derive a solution over time to spatial homogeneity. Particles will move from regions of high chemical potential to low ones. The questions in how long will it take.




First we have to derive what the flux of material is at each point in the solution.



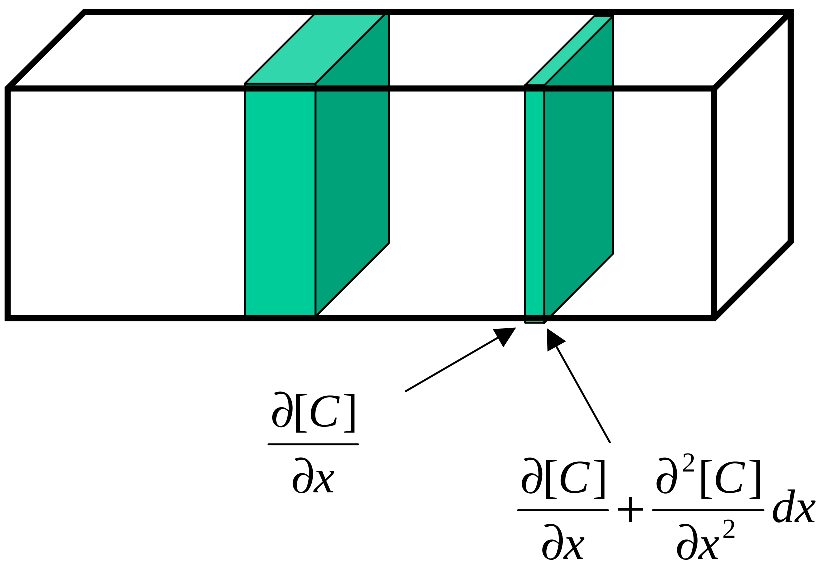



What is found experimentally is that:

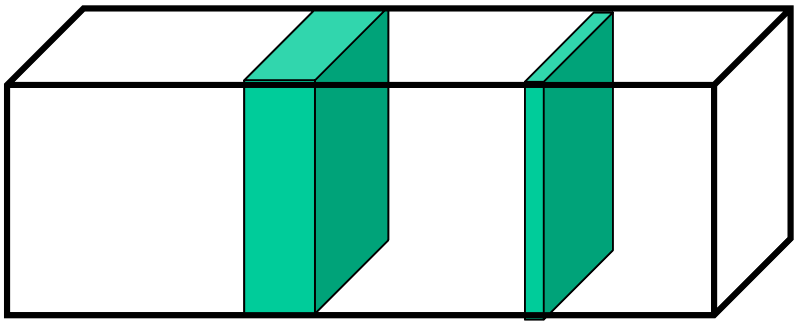
$$J_x \propto A\frac{\partial[C]}{\partial x}$$

$$J_x = -DA\frac{\partial[C]}{\partial x}$$

Fick’s First Law




In a small element, the rate of accumulation of material is the flux in minus the flux out.



$$\frac{\partial[C]}{\partial x}$$

$$\frac{\partial[C]}{\partial x}+\frac{\partial^2[C]}{\partial x^2}dx$$

In a small element, the rate of accumulation of material is the flux in minus the flux out.

Rate of entry at x= $$J_x = -DA\frac{\partial[C]}{\partial x}$$

Rate of entry at x + dx= $$J_{x+dx} = -DA\left(\frac{\partial[C]}{\partial x}+\frac{\partial^2[C]}{\partial x^2}dx\right)$$

Rate of Accumulation $$= DA\left(\frac{\partial^2[C]}{\partial x^2}dx\right) = DV_{slice}\frac{\partial^2[C]}{\partial x^2}$$

$$\boxed{\frac{d[C]}{dt} = D\frac{\partial^2[C]}{\partial x^2}}$$

Fick’s second Law

$$\boxed{\frac{d[C]}{dt} = D\frac{\partial^2[C]}{\partial x^2}}$$

Fick’s second Law

Fick’s second law gives us a relationship between the changing concentration gradient and the time dependence concentration.

Solutions to this equation are well-known!

$$[C] = \frac{const}{t^{1/2}} e^{-x^2/4Dt}$$

Given the original amount of starting material, N, normalization gives us the const.

$$N = \int_{-\infty}^{\infty} c\,dx \quad \Rightarrow \quad const = \frac{N}{2(\pi D)^{1/2}}$$

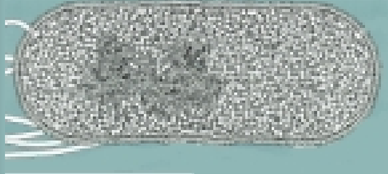
$$[C] = \frac{N}{2(\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

From this equation it is possible to calculate the amount of material at any volume element, at any position and at any time!

The mean square displacement of a concentration element can simply be calculated from this equation as well!

We know that the amount of a diffusing substance that reached x+dx from x is c*dx. Thus, the mean square displace of this material is:

$$< x^2 > = \frac{1}{N} \int_{-\infty}^{\infty} x^2 c dx = 2Dt$$



Thought problem:

Axons of a nerve cell are long processes that can extend more than 1 meter for nerve cells that connect to muscles or glands. If an action potential starting in the cell body of the neuron proceeds by diffusion of $Na^+$ and $K^+$ to the synapse, how long does it take the signal to travel 1m?

$$D_{25°C}(Na^+) = 1.5*10^{-5}\ cm^2/sec$$
$$D_{25°C}(K^+) = 1.9*10^{-5}\ cm^2/sec$$

a) 1 microsec b) 1msec c) 1sec d) 1min e) 1hr f) 1yr

Why is the diffusion constant of $Na^+$ less than that of potassium?

The diffusion coefficient of a particular molecule depends on its molecular parameters.

1) Size
2) Shape
3) Solvation
4) Flexibility

just to name the major ones.

There are thermal forces in any solution that resist the tendency for a particle to move.

Frictional forces are those that depend on the velocity of a particle.

Frictional force= $f$*u

Einstein proved in his Ph.D. thesis:

$$D = \frac{kT}{f}$$

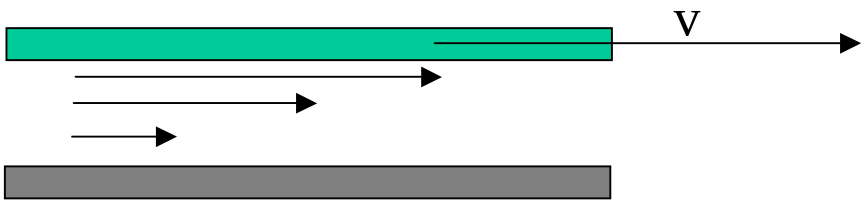
Stokes showed that it was possible to calculate $f$ for a spherical particle.

$$f = 6\pi\eta r$$

r= radius of sphere
$\eta$= viscosity of medium.

These sorts of calculations allow us to relate macroscopic measurement to microscopic parameters.

***Viscosity***




Viscosity is due to momentum transfer between differentially moving layers. The first layer next to the moving wall experiences a shear force:

$$F_{sh}=\eta A\, dV/dy$$

The $\eta$ here is the viscosity of the solution. The specific viscosity is defined as

$$\eta_{sp} = \frac{\eta' - \eta}{\eta}$$

where $\eta$’ is the viscosity of the pure solvent.

The intrinsic viscosity is the limit of specific viscosity as the solute goes to zero! This is dependent *only* on the molecular size and shape of the solute.

We can now begin to use our understanding of transport properties both to measure molecular parameters of macromolecules and to separate macromolecules from each other.

Consider sedimentation:

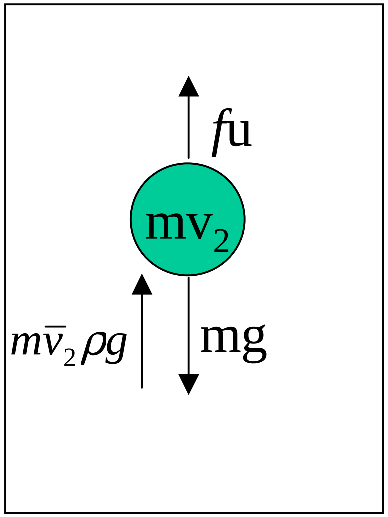
In sedimentation a particle is subject to gravity and falls under its influence. However, there is also a buoyant force!

(Thought problem: A toy metal cannon falls off a toy boat in a full bathtub. Does the water level go up or down?)

So the forces on the particle are

gravity= mg buoyant force= $m\bar{v}_2\rho g$

Where m is the particle mass, g is the gravitational force, ρ is the density of the viscous medium and $v_2$ is the partial specific volume.



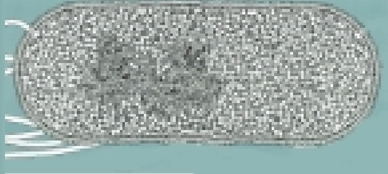

And, of course, there's friction!

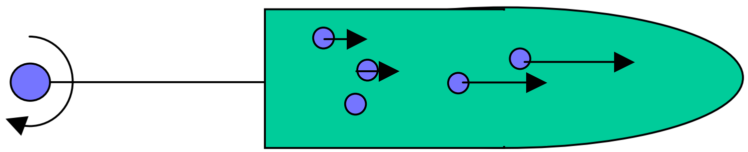
Since F=ma, we get for the total

$$m\frac{du}{dt} = m(1-\bar{v}_2\rho)g - fu$$

Since friction increases with velocity at some point the last term balanced the first and there is zero force on the particle. Thus, the particle stops accelerating.

In a centrifuge, instead of gravity, we use $m\omega^2 x$

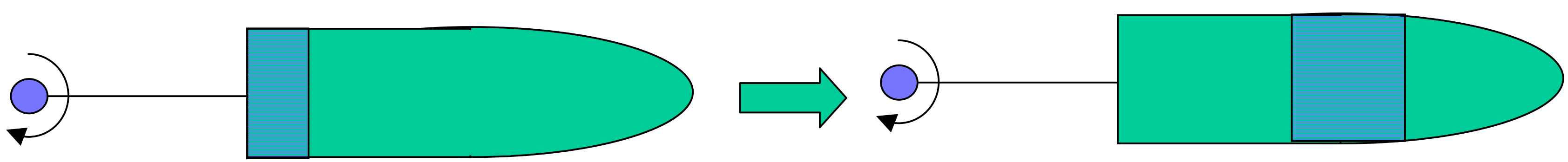




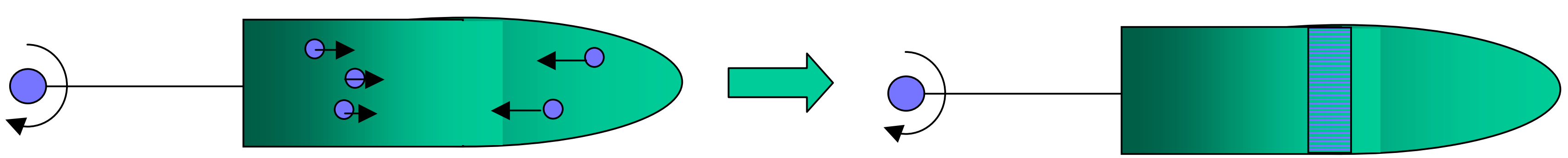
$$m\frac{du}{dt} = m(1-\bar{v}_2\rho)\omega r - fu$$

As the centrifuge spins, the particles will be forced to the bottom. Measuring dr/dt gives a measure of molecular weight.

Band Centrifugation: Also get D!

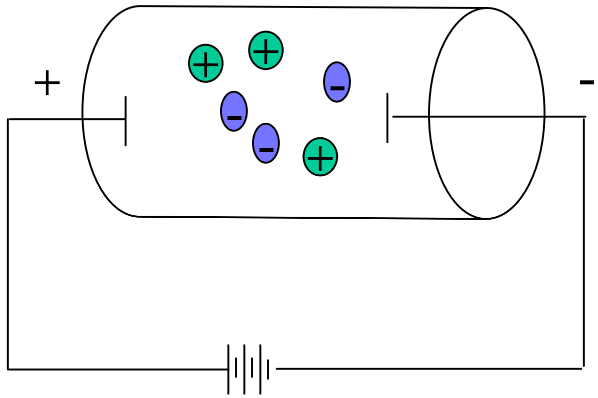


Density Centrifugation



Electrophoresis:

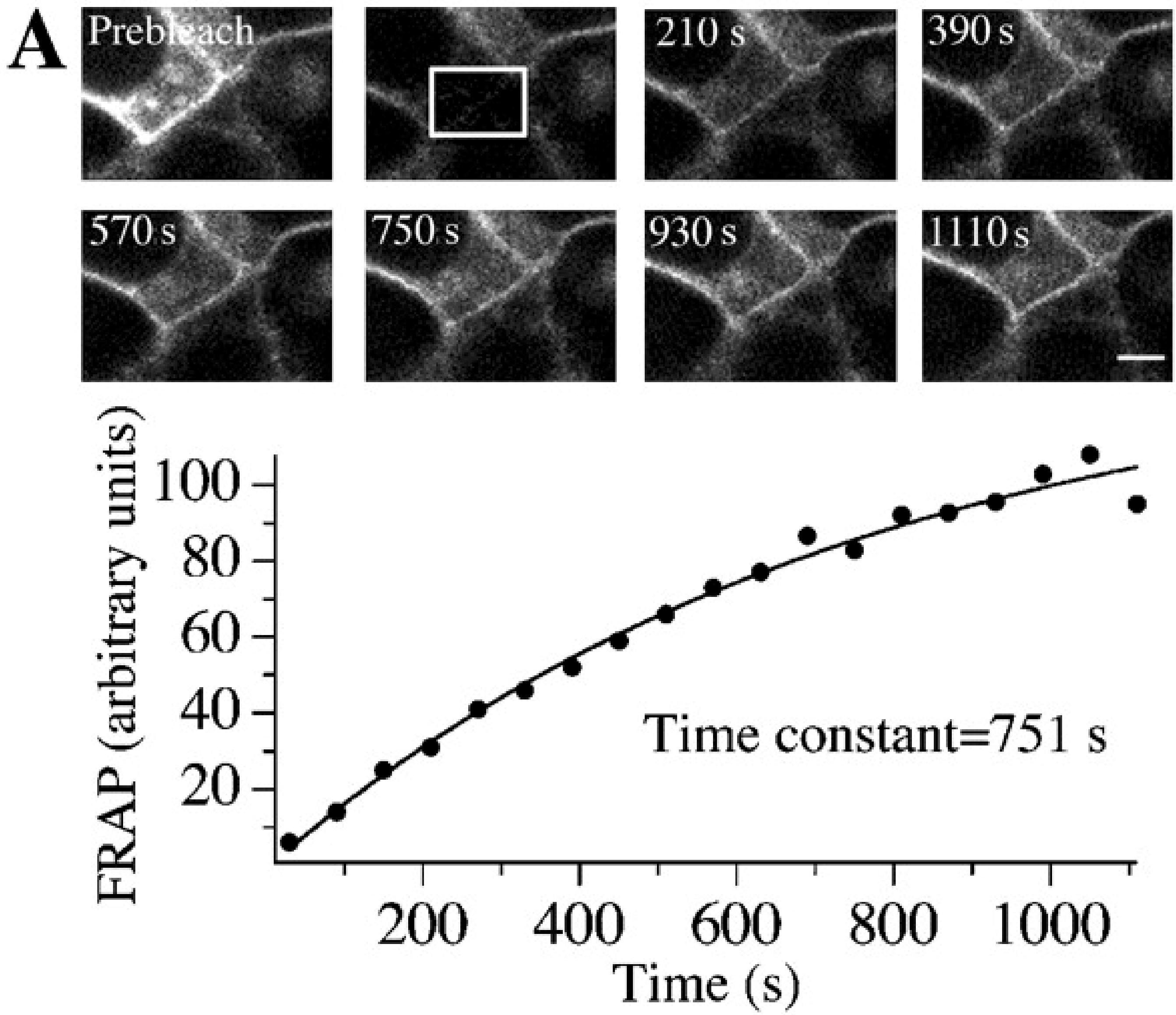
In electrophoresis, instead of the force being gravitational or centrifugal there is a field.



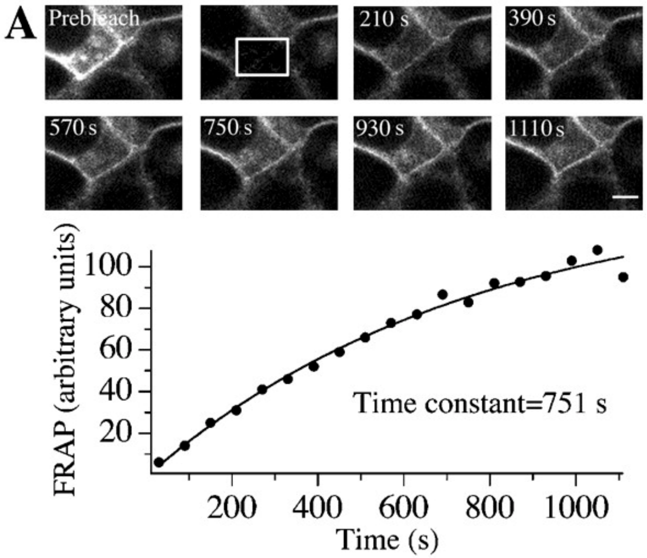

Must maintain charge neutrality throughout tube. So mobile macromolecules displace small ions and tend to bunch up together.

In Isoelectric focussing there is a pH gradient in the tube so the charge of the protein changes with where it is. When its charge is neutralized it no longer moves in the electric field.

| Transport Property | Anisotropy (Gradient) | Forces | Law | MW Dependence (Spherical Particles) |
|---|---|---|---|---|
| Diffusion | Concentration<br>T, $P_i$ | Diffusional$\rightarrow$<br>Frictional$\leftarrow$ | $J_x = -D\dfrac{dc}{dx}$ | $D \propto M^{-1/3}$ |
| Sedimentation Velocity | Centrifugal Acceleration | Centrifugal $\rightarrow$<br>Buoyant $\leftarrow$<br>Frictional $\leftarrow$ | $\dfrac{dr}{dt} = \dfrac{m\omega^2 r(1-\bar{v}_2\rho)}{f}$<br>$s = \dfrac{M(1-\bar{v}_2\rho)}{fN_A}$<br>$= \dfrac{MD(1-\bar{v}_2\rho)}{RT}$ | $s \propto M^{-2/3}$ |
| Sedimentation Equilibrium | Centrifugal Acceleration, Concentration | Centrifugal $\rightarrow$<br>Buoyant $\leftarrow$<br>Diffusional $\leftarrow$ | $M^{app} = \dfrac{RT}{(1-\bar{v}_2\rho)\omega^2 rc}\dfrac{dc}{dr}$ | |
| Viscosity | Velocity | Shear $\rightarrow$<br>Frictional $\leftarrow$ | $F_{sh} = \eta A\dfrac{du_x}{dy}$ | $[\eta] \propto M$ |
| Electrophoresis | Electric Field | Electrostatic $\rightarrow$<br>Frictional $\leftarrow$ | $u = \dfrac{Ze\varepsilon}{f}$ | |
| Rotary Diffusion | Shape | Rotational<br>Frictional | $\dfrac{d\Omega(\theta, f, t)}{dt} = D_{rot}\nabla^2\Omega(\theta, f, t)$ | |

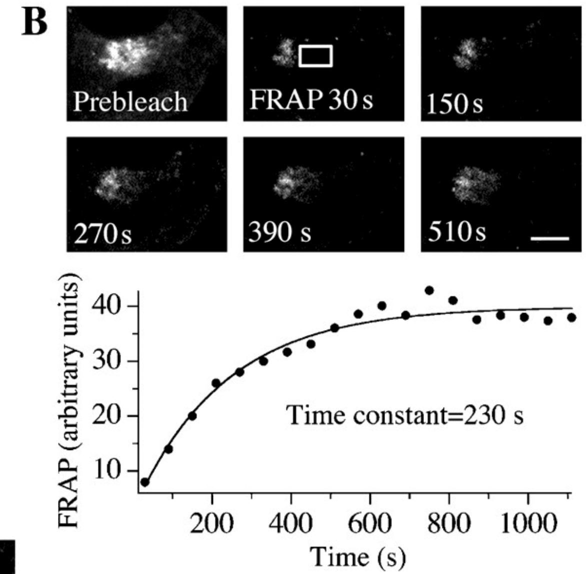

A
Prebleach
210 s
390 s
570 s
750 s
930 s
1110 s
FRAP (arbitrary units)
100
80
60
40
20
200
400
600
800
1000
Time (s)
Time constant=751 s

# Trafficking of Endothelial Nitric-Oxide Synthase

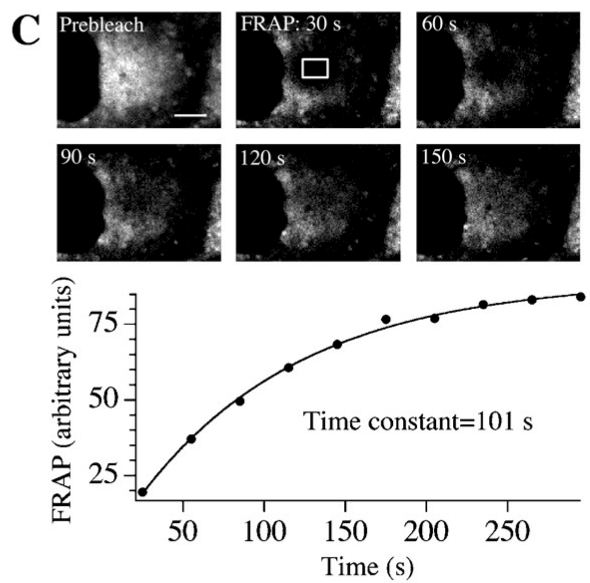



Plasma Membrane

Grzegorz Sowa, *et al.*, (1999)
Journal of Biological Chemistry
274(32), p. 22524




Golgi




Perinuclear Region

**Phase Equilibria**

**Binding Equilibria**

- Scatchard
- Cooperativity
- Donnan Effect

**Total Chemical Potential**

- Surface Tension
- Electrical
- Gravitational
- Centrifugal

**Transport**

- Active and Passive

**Colligative Properties**

- Ebulioscopy
- Cryoscopy
- Osmotic Pressure
- Raoult’s vs. Henry’s Law
- Molecular Weight Determination

**Kinetic Theory**

- Maxwell Boltzmann
- Mean Free Path